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Potential Impacts of Forest Herbicide Applications on California's Native American Basketweavers

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TABLE OF CONTENTS

Tables of Figures

Potential Impacts of Forest Herbicide Applications on California's Native American Basketweavers

Executive Summary

Background: The California Department of Transportation (CalTrans), the U. S. Forest Service (USFS), and many other federal, state and local agencies use herbicides to control plant growth on public lands. Vegetation management, as this control system is called, also includes mechanical, manual, thermal and biological removal of undesirable plants. Herbicide products used on California's national forests include clay pellets and liquids containing hexazinone (Pronone®, Velpar®), glyphosate (Accord®) and triclopyr (Garlon®).

Native Americans gather, process and use native plants for food, medicine and as materials to weave traditional baskets. Gathering occurs on private land, in national forests and sometimes near public roads and waterways. Without communication between those who gather and those who plan vegetation control, unwanted exposures to herbicides may occur. Those who gather traditional material seek to avoid exposure.

Native American gatherers felt a need for additional information on herbicide spraying activities. They informed government agencies of a desire to improve communication. In addition, many individuals believed these herbicides presented a health hazard. Our examination of environmental impact statements produced by the Pacific Southwest Region of the USFS and CalTrans found no specific estimates of exposure to Native American gatherers. Therefore, the US Environmental Protection Agency, the USFS and the Cal/EPA Department of Pesticide Regulation (DPR) are studying the issue through these and other research efforts.

Scientific models and environmental monitoring data allowed DPR staff to begin exposure estimation. Pronone® 10G, a granular hexazinone formulation is a common forestry herbicide. Environmental monitoring data was collected by the Environmental Monitoring and Pest Management Branch. Applications of hexazinone in the Pronone® formulation provided concentrations of the herbicide in plants. The plants selected were important to

Native gatherers in Northern California. These concentrations helped DPR estimate exposure and test model reliability.

Scientific models like CalTOX™ also served as tools in exposure assessment. CalTOX™ includes a series of exposure and chemical breakdown calculations. The scientific models were especially valuable in this assessment because no specific studies on herbicide exposure to Native American gatherers are available. Both monitoring and modeling improved the exposure assessment estimations.

This report summarizes the assessment of CalTOX™ as a viable exposure model for forest herbicides and reports preliminary estimates of exposure. Later reports will include more complete exposure estimates.

Objectives: 1) Test the scientific model CalTOX™ for reliability. Specifically, DPR tests how well CalTOX™ predicts pesticide movement into air, surface water sediment and plants. 2) Make preliminary estimates of basketweaver exposure to granular hexazinone (Pronone® 10G) used in national forests.

Methods: Hexazinone uptake into plants and movement through the environment was measured in several field studies. The scientific model CalTOX™ estimated both plant uptake and movement of hexazinone in a simulated environment. Results of model estimates were compared to field measurements.

Using the results of environmental movement of hexazinone in a simulated environment, DPR estimated exposure from contact to hexazinone. Human contact is predicted by the model. The worst-case assessment assumed an individual lived very near forest application sites. Exposure estimates were compared to Environmental Protection Agency standards for exposure.

Major Findings: 1) Based on comparisons to field data, the scientific models provided reasonable estimates of hexazinone levels in the environment. 2) The U. S. EPA health standard, the acceptable daily intake (0.033 mg/kg-d) was 1,000 to 10,000 times higher than estimates of exposure to granular hexazinone.

Interim Report

Potential Impacts of Herbicides on Northern California Native American Basketweavers

Background

Basketweavers and CIBA

The California Indian Basketweavers Association (CIBA) formed in 1992. This occurred after a gathering of a diverse group of individuals for the first time in 1991. From Del Norte and Trinity to Mono and Inyo counties, men and women discussed common issues about the art of gathering native plants and weaving baskets. Foremost among these issues was obtaining access to plant harvesting areas free from management practices involving the use of pesticides. Consequently, CIBA members brought access and safety problems to the attention of State and Federal authorities.

CIBA members desire pesticide-free plant materials. However, few plants exist free of long-range chemical deposition or natural insecticidal, anti-bacterial or anti-germination chemical compounds. In addition to re-deposited and intrinsic pesticide chemicals, however, pesticides are applied directly to forest plants through vegetation management practices. These practices include spraying to maintain rights of way, ditches and wood production goals. Without an adequate dialogue between regulators and traditional gatherers, the members of CIBA feel these activities present a random and ill-defined hazard.

A Dialogue with Regulators

Members of the Environmental Monitoring and Pest Management Branch (EM&PM) of the California Environmental Protection Agency (Cal/EPA) met with several tribal representatives and compiled a list of culturally important plants. The following list includes the *botanical name*, common name and the plant part of interest to weavers and gatherers:

1. *Anaphalis margaritaceae* (pearly everlasting-foliage)
2. *Arctostaphylos spp.* (manzanita-berries)
3. *Ceonothus cuneatus* (buckbrush-shoots)
4. *Ceanothus intergerrimus* (deer brush-shoots)
5. *Clorogalum pomeridianum* (soaproot-bulb)
6. *Cornus spp.* (dogwood-shoots)
7. *Ericamera arborescence* (golden fleece-foliage)
8. *Muhlenbergia rigens* (deergrass-stalks)
9. *Prunus emarginata* (bitter cherry-shoots)
10. *Pteridium aquilinum* (bracken fern-rhizome)
11. *Quercus spp.* (oak-acorns)
12. *Rorippa nasturtium-aquaticum* (watercress-foliage)
13. *Salix spp.* (willow-shoots)
14. *Sambucus spp.* (elderberry-berries)

The basketweavers' fear of the consequences of pesticide contact is amplified through personal, oral accounts of blistering, illness, and cancer. Many weavers associate personal accounts of mouth swelling and blistering with plant contact (CIBA, 1996; Perez-Kelley, 1997). Instead of the written word, most of California's original inhabitants used oral, histories before the arrival of Europeans in North America. This oral tradition remains in today's Native American culture. This tradition lends significant value to verbal accounts of illness.

Because of these fears, CIBA members declined participation in exposure monitoring (Greensfelder, 1995). Subsequent discussion of exposure concerns with Federal and State agencies, however, revealed a willingness to begin a dialogue. This exposure assessment attempts to evaluate the magnitude of herbicide exposure due to gathering and weaving. The results will assist the US Forest Service (USFS), the United States Environmental Protection Agency (U. S. EPA) and Cal/EPA in exposure mediation discussions with Native Californians.

Government Policy and Protecting Gathering Sites

The U. S. EPA, USFS and the California Department of Transportation (CalTrans) all have specific regulations and directives which spellout how agencies are to handle and prioritize Native American concerns. On April 29, 1994, President Clinton issued a memorandum to the U. S. EPA. Among other things it outlines the government-to-government nature of Native American-US relations and the importance of maintaining an

"open and candid" dialogue when "taking actions that affect federally recognized tribal governments" (Clinton, 1994). This also includes, "assess(ing) the impact of Federal Government plans, projects, programs, and activities on tribal trust resources and assur(ing) that tribal government rights and concerns are considered during the development of such plans, projects programs and activities" (Clinton, 1994). The Executive Branch mandates cooperation and communication for the U. S. EPA.

Regulations similar to U. S. EPA rules apply to vegetation managers in California. The USFS and CalTrans have clear guidelines about providing access to undisturbed gathering areas. The USFS guidelines state "Native American collection areas . . . will be identified and protected from vegetation management and timber sales by redesigning and rescheduling project activities to avoid conflicts between Native American use and Project objectives" (U. S. EPA, 1988). CalTrans policy reads, "(Managers will) establish a process to avoid or adjust the timing of spraying populations of native plants used by Native Americans" (CalTrans, 1992). Both agencies are likely to affect traditional gathering areas.

Gathering area impact occurs because private landowners, USFS, CalTrans, and many other agencies spray pesticides in order to manage rights-of-way (roadsides, power line thoroughfares) and forest tree growth in California. Table 1 presents forest and right-of-way use of triclopyr, hexazinone and glyphosate by the USFS in the four national forests where herbicide management is practiced (USDA, 1992; USDA, 1993; USDA, 1994; USDA, 1995; USDA, 1996). The data is provided from USFS reports of use. Table 1 data is presented in units of pounds of active ingredient per acre (lbs. ai/acre; triclopyr and its ester) for four years (1993-1996) and the total use in all of California's national forests (last column).

In Table 2, herbicide use throughout the state is summarized (DPR, 1997). This data comes from California's pesticide use reporting system. The number of acres treated along rights-of-way is estimated from application rates (glyphosate, triclopyr) reported by CalTrans (CalTrans, 1991, pg. 3-56) and by labels (hexazinone) (DuPont, 1985). Reported California-wide forest applications (Table 2) amounted to 81,000 pounds of

triclopyr active ingredient in 1995 over 37,000 acres. This represents roughly half of the 161,000 pounds of triclopyr applied for all uses (DPR, 1997). Applications in the national forests, however, represent just a fraction of these applications. In 1995, triclopyr applications totaled approximately 6000 lbs. of active ingredient in national forests (Table 1), 7% of total triclopyr use in California's forests (DPR, 1997).

Table 1. Herbicide use in California's national forests, 1993-1996

Herbicide	Year	Lassen (lbs. a.i.)*	Eldorado (lbs. a.i.)*	Stanislaus (lbs. a.i.)*	Sierra (lbs. a.i.)*	Sum of CA Nat'l Forests (lbs. a.i.)*
Hexazinone	1993	3450	9360	0	343	13160
	1994	765	2440	0	0	3210
	1995	675	69	808	75	1630
	1996	192	0	10339	146	10700
Glyphosate	1993	0	2864	1593	50	4920
	1994	0	562	2645	1930	5330
	1995	714	8180	1480	716	11300
	1996	0	1940	8400	1720	12600
Triclopyr	1993	0	839	217	0	1060
	1994	0	560	167	0	730
	1995	703	5130	126	0	5960
	1996	0	3750	313	0	4840

* pounds of active ingredient

Table 2. Herbicide use in California, 1995

Herbicide	Use	Forest Trees, Forest Lands	Rights-of-Way	Estimated lbs. ai /acre*
Hexazinone	lbs. used	47021	41	1.5
	acres treated	11783	**27	
Glyphosate	lbs. used	30775	1072400	2
	acres treated	25640	**536200	
Triclopyr	lbs. used	81016	40700	3
	acres treated	37413	**13600	

*pounds of active ingredient per acre
**estimated from use rate and lbs. of AI used

Table 2 shows glyphosate use on rights-of-way in California is substantial. Roadways or powerlines near gathering sites increase the chances of exposure to glyphosate considerably as more than a million pounds are sprayed yearly, statewide (Table 2).

Cultural issues about the location of gathering sites created problems designing a mitigation strategy. The USFS and CalTrans have proposed to curtail spraying near gathering areas. However, many gathering sites are considered sacred. Their locations are shared with family weavers but not generally shared with other tribal or non-tribal members. Native Americans carefully tend gathering areas through cutting, planting and burning (Parker, 1997). These management techniques have been practiced for hundreds of years (Bibby, 1996). This tradition lends sacred value to sites which includes a necessary desire to protect gathering locations. A comprehensive plan to address this issue has not been brokered.

Exposure Assessment

Health concerns led the USFS and the U. S. EPA to contract with the DPR to evaluate the situation. DPR developed a two-pronged approach. First, the EM&PM Branch produced a list of traditionally gathered plant materials with the aid of California Native gatherers. EM&PM then developed a field sampling and analysis regime for fourteen plant types in four national forests (Stanislaus, Eldorado, Sierra or Lassen). Field study personnel collected plant material for analysis of glyphosate, triclopyr, or hexazinone total plant residues after prescribed spraying events. EM&PM collected samples for residue levels during the spring and summer months of 1997 and 1998.

Concurrent to monitoring, DPR Worker Health and Safety (WH&S) personnel began the exposure assessment project. Estimating exposure usually involves (1) monitoring body wastes or clothing of exposed individuals or (2) video analysis of exposure events. Native gatherers declined participation in these studies. Therefore, without human monitoring, exposure assessment is indirect. The assessment included the following steps:
(1) A herbicide chemical properties assessment including mobility, reactivity, and use practices which affect exposure; (2) a human activities assessment of the rate and extent of Native American gatherer contact with soil, air, water and plants; (3) a site assessment of climate and soil parameters; (4) a calculation of herbicide dispersion from the application site into environmental media (soil, air, water and plants) and (5) an estimation of the contact rate with impacted media. Taken together these steps approximate the total chemical contacting an exposed individual over time; this is the estimated potential exposure.

The following describes initial estimates of the environmental fate of hexazinone in a northern California setting and aspects of exposure relevant to basketweavers in national forests. Specifically, progress in the exposure assessment includes the following:

1) Development of a pesticide properties database for hexazinone
2) A database comparison of DPR library resources to on-line physico-chemical data
3) A series of CalTOX™ model (McKone, 1994) simulations that estimated environmental transport and transformation of hexazinone
4) A scientific model evaluation testing the validity of the CalTOX™ model simulation against field data
5) The identification of plant dermal contact and ingestion as a significant source of potential exposure to traditional Native American gatherers

Potential Impacts Assessment for California's Native American Gatherers

In order to assess the exposure of Native American gatherers to herbicide residues, we first estimate how the sprayed contaminant reaches the exposed individual. These estimates include how the chemical moves between environmental compartments (transport) and how it degrades or becomes bound (transformation). Exposure and intermedia transport and transformation estimates require developing a method to assess chemical movement and degradation in a variety of environments. In other words, we require a scientific model in which changing exposure scenarios result in correspondingly different exposures. Exposure scenarios are a description of the conditions (location, time, chemical state, human activities, etc.) during which exposure occurs. The model CalTOX™ meets these criteria.

An Environmental Fate and Human Exposure Model-CalTOX™

The CalTOX™ model, developed at the Lawrence Livermore National Laboratory and the University of California at Davis, contains a multiple media transport and transformation model, exposure scenario models, and methods to quantify and reduce uncertainty in

multimedia, multiple-pathway exposure models. At the California Department of Toxic Substances Control (DTSC), CalTOX™ serves to estimate risk to persons living near Superfund sites and to calculate soil clean-up goals. With CalTOX™, DPR has a tool to predict the extent of contamination in environmental media (soil, air, surface water, sediments, and ground water) in a variety of environments. The route of human exposure is through media contact. Figure 1 illustrates the interactions between environmental media, exposure media, and exposure routes [McKone, 1993 #342].

DPR chose CalTOX™ for this assessment because of its flexibility in defining the environment and its comprehensive exposure model. CalTOX™'s developers were concerned with potentially harmful levels of contaminants at very low concentrations. This concern comes from experience with pollutants that accumulate in food products through magnification in the human food chain (e.g. soil→plants→cows→milk→humans). As most herbicides are not likely to bioaccumulate, the exposure model is conservative with its approach to potential exposure.

In addition to the suitability of the exposure model, CalTOX™ was chosen because pesticide-impacted sites are comparable to areas managed by DTSC. The resemblance stems from the way pollutants become distributed in the environment. For both kinds of contamination, the soil environment is often the original source of potential exposure. From soil, the pesticides then distribute into adjacent environmental media. CalTOX™ allows us to define this landscape using dozens of descriptive parameters.

The exposure model is demonstrated, in part, by the information in Table 3. CalTOX™ uses unique pathways from dust, poultry, mothers' milk and others to ensure inclusion of many potentially significant exposure routes. The air to fruit pathway, for example, implies the deposition of contaminated air and dust particles (air *source*) onto fruit (ingestion *route*).

CalTOX™ assists the user in examining how chemical and landscape properties impact both the ultimate route and quantity of human contact. The model allows the user to determine whether a substance (a) remains or accumulates within the compartment [e.g. air or soil] of its origin, (b) transforms physically, chemically, or biologically within the

compartment of its origin (i.e., by hydrolysis, oxidation, etc.), or (c) transports to another compartment by cross-media transfer that involves chemical movement (i.e., evaporation, diffusion, etc.)

Exposure assessment includes measuring and/or estimating the concentration of contaminant in the media reaching the exposed individual. Whether it is water, air, soil or food, the contaminant level in the exposure medium defines the potential exposure. The CalTOX™ model uses multiple media (air, water, food and soil) and multiple exposure pathways (e.g. from soil to air then inhaled into the lung), to perform these exposure estimates.

Models are simply tools, ideally used in combination with field data and other information to assess possible impacts to individuals. Models validated by field analyses provide more confidence in estimates of exposure. However, they do not work well in every situation. Models merely assist us in combining large numbers of calculations previously accomplished by hand. Results of model simulations are then used as one piece of a large puzzle. Each piece contributes information needed to choose how to estimate hazards to individuals. Risk managers also include field analyses, public perception, and risk/benefit analyses as parts of any risk management decision.

Data Needs for CalTOX™

CalTOX™ uses three sets of input data to estimate the fate of a chemical and human exposure to it. Input data set one describes the chemical-specific properties of the contaminants (Table 4). A second set provides properties of the environment or landscape receiving the contaminants (Table 5). The final data set, exposure parameters (Table 6), defines (for exposure assessment) the characteristics of individuals in various age/sex categories and the characteristics of the microenvironments in which they live or from which they obtain water and food.

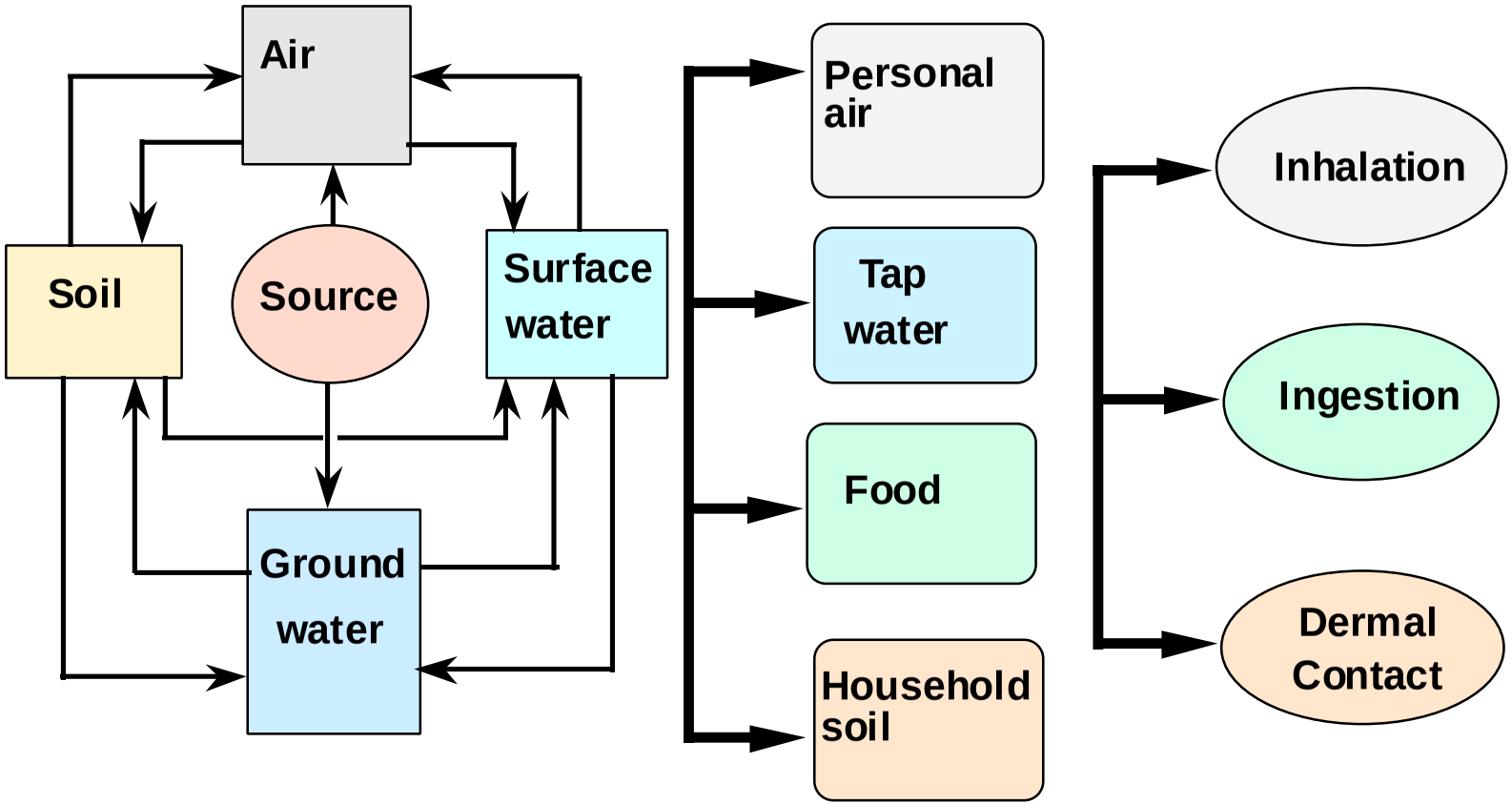

Figure 1. The potential interactions among source term, environmental media, exposure media, and exposure routes that must be addressed in a multimedia, multiple pathway, exposure assessment.

Table 3. Matrix of exposure pathways linking environmental media, exposure scenarios, and exposure routes.

Exposure Routes	***Media***		
	Air (gases and particles)	**Soil (surface soil and root-zone soil)**	**Water (surface water and ground water)**
Inhalation	• Inhalation of gases and particles in outdoor air • Inhalation of gases and particles transferred from outdoor air to indoor air	• Inhalation of soil vapors that migrate to indoor air • Inhalation of soil particles transferred to indoor air	• Indoor inhalation of contaminants transferred from tap water
Ingestion	• Ingestion of fruits, vegetables, and grains contaminated by transfer of atmospheric chemicals to plant tissues • Ingestion of meat, milk, and eggs contaminated by transfer of contaminants from air to plants to animals • Ingestion of meat, milk, and eggs contaminated through inhalation by animals • Ingestion of mothers milk	• Human soil ingestion • Ingestion of fruits, vegetables, and grains contaminated by transfer from soil • Ingestion of meat, milk, and eggs contaminated by transfer from soil to plants to animals • Ingestion of meat, milk, and eggs contaminated through soil ingestion by animals • Ingestion of mother's milk	• Ingestion of tap water • Ingestion of irrigated fruits, vegetables, and grains • Ingestion of meat, milk, and eggs from animals consuming contaminated water • Ingestion of fish and sea food • Ingestion of surface water during swimming or other water recreation • Ingestion of mother's milk
Dermal contact	(not considered) hexazinone does not have sufficient volatility	• Dermal contact with soil	• Dermal contact in baths and showers • Dermal contact while swimming

Chemical-Specific Properties

Chemical-specific properties consist of physicochemical properties, distribution coefficients, biotransfer and bioconcentration factors, and chemical transformation rates. Each chemical behaves uniquely in each set of parameter categories. Physicochemical properties include molecular weight (MW), octanol-water partition coefficient (K_{ow}), melting point (MP), vapor pressure (VP), Henry's law constant (H), diffusion coefficients in air (D_{air}) and water (D_{water}), and the organic-carbon partition coefficient [K_{oc}] (see Appendix B). These properties help predict where an organic chemical prefers to remain in the environment and how fast it will get there; whether it prefers organic material, water, or air.

Distribution coefficients (solid/water) describe what fraction of the chemical will remain on a solid (soil or sediment particles) or in the solution between particles. The sorption coefficient, K_d, is the equilibrium concentration ratio of chemical adsorbed or absorbed to solids (mol/kg) and the chemical concentration in the solution, mol/L. When the octanol/carbon sorption coefficient (K_{oc}) is multiplied by the fraction organic carbon (f_{oc}) in a soil or sediment, we obtain an estimate of the soil/water or sediment/water partition coefficient {$K_d = K_{oc} \times f_{oc}$}

Biotransfer and bioconcentration parameters are similar to distribution coefficients except that the chemical is partitioning between a biological phase and many other phases. The CalTOX™ model requires general relationships that can be used to estimate partition coefficients. The media partitioning occurs between air and plants, soil and plants, animal feed intake and animal-based food products, surface water and fish, etc. (see Table 4).

Chemical transformations, which may occur as a result of biotic or abiotic processes, can have a profound effect on the persistence of contaminants in the environment. Specific information on the rates and pathways of transformation for individual chemicals of concern should be obtained directly from experimental determinations, if possible, or derived indirectly from information on chemicals that are structurally similar.

Landscape Data

Because it is often impractical to develop detailed parameter sets for the landscapes surrounding a large number of gathering sites, we have chosen landscape data sets that are representative of north central California (Table 5). Examples of the types of data needed to construct a landscape data set include meteorological data, hydrologic data and soil properties. Meteorological data examples include average annual wind speed, deposition velocities, and air temperature. Hydrologic data may include annual rainfall, runoff, soil infiltration, ground-water recharge, and surface water depth. Soil properties include bulk density, porosity, water content, erosion rates, soil root-zone depth, etc.

Exposure Data

In constructing exposure models one needs to define the characteristics of individuals and the characteristics of the microenvironments in which they live or from which they obtain water and food (Table 6) (McKone, 1993a). This data often takes the form of a contact frequency (hours/day, days/year) and an amount of material contacted (liters, kilograms). Then, in combination with a concentration (mg chemical/kg media) and a body weight (kg body weight), the exposure is calculated. The equation yields mass of chemical contacted per body mass unit per day (mg chemical/kg (bodyweight)/day), known as the average daily exposure (ADE).

$$\textbf{ADE (mg/kg-d)} = \frac{\frac{kg \text{ of "soil"}}{\text{day}}\left(\frac{x \text{ mg of chemical}}{kg \text{ of "soil"}}\right)\left[\left(\frac{8\ hours}{24\ hours}\right)\left(\frac{200\ days}{year}\right)(30\ years)\right]}{70\ kg \text{ bodyweight}\left[\left(\frac{365\ days}{year}\right)(30\ years)\right]}$$

CalTOX™ uses a large number of input parameters, which appear cumbersome to conducting timely risk evaluations. However, each factor has the potential to affect exposure significantly. Therefore, the model requires a large number of parameters. In practice, we use "first cut" data to evaluate an exposure scenario then improve the more *sensitive* data. In other words, we select average values taken from a few chemical property measurements or descriptions of large geographic areas. From this initial data, a process called *sensitivity analysis* tells us which parameters (e.g. rainfall, water solubility)

affect the outcome (exposure estimate) most strongly. Model users then obtain more accurate numbers for those *sensitive* parameters. For example, if rainfall was a sensitive parameter, we would characterize the rainfall for that watershed, replacing a default value selected from regional statistics. More accurate values from sensitive parameters reduce the total variability in the estimation. This process may not take long as a few variables often affect the model result strongly. Choosing which data to collect is the key to calculating exposures that make sense. Realistic estimations provide another tool to make appropriate decisions concerning individual health.

Exposure Analysis using CalTOX™

We estimated the contact rate with individuals using chemical, landscape and exposure parameters (Tables 4-6). We gathered chemical specific information as our first step. Each chemical has unique properties that define its mobility, toxicity and reactivity in the environment. Glyphosate, triclopyr and hexazinone possess unique characteristics. Hexazinone served as a test case for physical and chemical data gathering. We summarized data culled from the open literature, USFS reports and the DPR library. This data provided averages and estimates of 29 physical, chemical, intermedia transfer and half-life parameters (Table 4). Estimation methods for several intermedia transfer factors (see appendix A) developed from literature equations were used when measurements were not available (footnote 'e' in Table 4). Table 4 summarizes hexazinone's properties and includes a parameter description, its symbol, the arithmetic average value (mean value), coefficient of variation (CV), and the number of values used to create the average. Appendix A describes each parameter briefly.

Previously, the U. S. EPA defined exposure in terms of contact with the so-called "exchange boundaries" (Figure 2) where contaminant absorption takes place (skin, lung, gastrointestinal tract) (U. S. EPA, 1988). However, the more recent consensus of the scientific community differs from this definition. The NRC suggests that exposure should be defined in terms of contact with the visible exterior of the person (NRC, 1991; NRC, 1991; U. S. EPA, 1992). *Visible exterior* defined as the skin and openings into the body, such as mouth and nostrils. DPR uses the latter definition. Under this definition, we view

the human body as having a hypothetical outer boundary separating internal living tissues from the outside surfaces. This outer boundary is the skin and openings to the body, such as the mouth, the nostrils, and skin punctures and lesions.

Dermal Contact

Initial discussions of the CalTOX™ exposure paradigm led us to conclude that an assessment of exposure to Native American gatherers requires additional emphasis on dermal exposure pathways. The following discussion highlights dermal pathways of exposure to plant material. We plan a separate assessment of dermal exposure due to its potential importance and to the limited treatment of dislodgeable residue by CalTOX™. We intend to add the exposure rate from these calculations into the total exposure estimated in CalTOX™.

Figure 2-Exchange Boundary

Native American basketweavers use tools and their hands to dig up roots and gather grasses and branches used for weaving (Voll, 1996). Processing often includes washing, splitting and soaking the materials; then drying for months to years (Wallace, 1996). The weaving material is soaked again prior to using the mouth and/or hands for weaving (Parker, 1997).

Dermal exposure happens during contact with soil, the plant interior (through hand and mouth processing), and dislodgeable residues on the plant surface. Soil contact during gathering is likely to be significant from both dust and direct contact. Due to high solubility, soil water may contain high levels of compound. Hexazinone, for example, has a granular formulation activated by rain.

Contact with the plant's internal residues may occur while cutting and processing the materials. For example, weavers strip willow branches of their bark and split it when fresh (Voll, 1996). Because hexazinone is a systemic herbicide, it is transported throughout the plant from the point of origin (roots or foliage). Internal residue concentrations can reach high levels (2 to 700 ppm) (DuPont, 1992). Results of field analyses in California showed much lower concentrations for the granular formulation of hexazinone, Pronone 10G [<1 ppm]. More significant concentrations were found in foliage and shoots impacted by the liquid formula Velpar [0-212 ppm] (Segawa, 1998). For a variety of plants, the measured half-life ranges from 20 to 90 days (39-day mean). This corresponds to a degradation rate constant (k) of 0.018 $days^{-1}$.

Dislodgeable residue exposure occurs when Native American gatherers contact surface contaminated plants. Contact occurs both during gathering and while walking through contaminated areas. This kind of contact varies with the plant collected, but compares well to documented activities of grape and fruit pickers. Hand and mouth contact to dislodgeable residues occurs during weaving. DPR has no quantitative measure of the time weavers spend traveling from roads to gathering sites, gathering plants, processing plant materials, or weaving. A range of values describing the frequency of these activities among weavers is necessary to estimate the oral and dermal exposure.

Table 4. Physico-Chemical and Intermedia Transfer Parameters

Description	Symbol[a]	Mean Value	CV	No. Values
Molecular Weight (g/mol)	MW	252.3	0.01	1
Octanol-Water Partition Coefficient	K_{ow}	15	0.04	3
Melting Point (K)	T_m	389.2	3.6×10^{-3}	2
Vapor Pressure (Pa)	VP	2.2×10^{-5}	0.34	3
Solubility (mol/m^3)	S	124	0.072	2
Henry's Law Constant (Pa-m^3/mol)	H -	2.0×10^{-7}	0.071	2
Diffusion Coefficient in Pure Air (m^2/d)	D_{air} -	0.68	0.080	e
Diffusion Coefficient in Pure Water (m^2/d)	D_{water} -	9.6×10^{-5}	0.25	e
Organic Carbon Partition Coefficient	K_{oc} -	83	2.1	6
Distribution Coefficient in Ground-Surface and Root-Zone Soil	K_{d_s} -	b	e	e
Distribution Coefficient in Vadose-Zone Soil	K_{d_v} -	b	e	e
Distribution Coefficient in the Ground-Water Zone	K_{d_q} -	b	e	e
Distribution Coefficient in Ground Water Sediment	K_{d_d} -	b	e	e
Partition Coefficient in Plants Relative to Soil Concentration {ppm (pFM)/ppm (sFM)}	K_{ps} -	1.2	2.3	12
Biotransfer Factor in Plants Relative to Contaminant Air Concentration (m^3{a}/kg{pFM})	K_{pa} -	6.7×10^{6}	14	e
Biotransfer Factor in Milk Relative to Cattle-Diet Contaminant Intake (d/kg)	B_k -	1.0×10^{-2}	5	1
Biotransfer Factor in Meat Relative to Cattle-Diet Contaminant Intake (d/kg)	B_t -	4.7×10^{-6}	13	e
Biotransfer Factor in Eggs Relative to Hen-Diet Contaminant Intake (d/kg)	B_e -	1.7×10^{-2}	5	1
Biotransfer in Breast Milk Relative to Contaminant Intake by the Mother (d/kg)	B_{bmk} -	3.0×10^{-6}	10	e
Bioconcentration Factor in Fish Relative to Contaminant Water Concentration	BCF -	6.0	0.24	2
Skin Permeability Coefficient (cm/h)	K_{p_w} -	3.7×10^{-3}	2.4	e
Skin-Water/Soil Partition Coefficient	K_m -	3	0.27	e
Reaction Half-Life in Air (d)	T_{half_a}	10	1.0	1
Reaction Half-Life in Ground-Surface Soil (d)	T_{half_g}	100	0.74	24
Reaction Half-Life in Root-Zone Soil (d)	T_{half_s}	100	0.74	24
Reaction Half-Life in the Vadose-Zone Soil (d)	T_{half_v}	100	0.74	24
Reaction Half-Life in Ground-Water Zone Soil (d)	T_{half_q}	110	0.89	3
Reaction Half-Life in Surface Water (d)	T_{half_w}	52	0.33	4
Reaction Half-Life in the Sediment (d)	T_{half_d}	110	0.89	3

[a]Values followed by a "-" include default equations that can be used for estimations

[b]K_d = {(K_{OC}) × (fraction organic matter)}, a site and soil zone specific parameter

[e]estimated parameter value

Table 5. Landscape properties

Description	Symbol	Mean value	CV
contaminated area in m^2	Area	1.00 E+06	0.1
annual average precipitation (m/d)	rain	2.23 E-03	0.067
flux; surface water into landscape (m/d)	inflow	3.92 E-04	0.1
land surface runoff (m/d)	runoff	3.30 E-04	1
atmospheric dust load (kg/m^3)	rhob_a	6.15 E-08	0.2
deposition velocity of air particles (m/d)	v_d	3.34 E+02	0.3
plant dry mass inventory ($kg\{DM\}/m^2$)	bio_inv	3.10 E+01	0.2
plant dry-mass fraction	bio_dm	3.30 E-01	0.2
plant fresh-mass density kg/m^3	rho_p	1.00 E+03	0.2
ground-water recharge (m/d)	recharge	1.20 E-04	1
evaporation of water from surface wtr (m/d)	evaporate	3.34 E-04	1
thickness of the ground soil layer (m)	d_g	1.00 E-02	1
soil particle density (kg/m^3)	rhos_s	1.30 E+03	0.05
water content in surface soil (vol fraction)	beta_g	4.50 E-01	0.2
air content in the surface soil (vol frctn)	alpha_g	2.00 E-01	0.2
erosion of surface soil (kg/m^2-d)	erosion_g	8.38 E-04	0.2
thickness of the root-zone soil (m)	d_s	1.52 E+00	0.2
water content of root-zone soil (vol. frctn.)	beta_s	2.80 E-01	0.2
air content of root-zone soil (vol. frctn.)	alpha_s	2.00 E-01	0.2
thickness of the vadose-zone soil (m)	d_v	5.00 E+00	0.1
water content; vadose-zone soil (vol. frctn.)	beta_v	3.00 E-01	0.2
air content of vadose-zone soil (vol. frctn.)	alpha_v	1.00 E-01	0.2
thickness of the aquifer layer (m)	d_q	3.00 E+00	0.3
solid material density in aquifer (kg/m^3)	rhos_q	2.60 E+03	0.05
porosity of the aquifer zone	beta_q	2.00 E-01	0.2
fraction of land area in surface water	f_arw	1.90 E-02	0.2
average depth of surface waters (m)	d_w	6.00 E+00	1
suspended sedmnt in surface wtr (kg/m^3)	rhob_w	3.40 E-01	1
suspended sdmnt deposition (kg/m^2/d)	deposit	1.05 E+01	0.3
thickness of the sediment layer (m)	d_d	5.00 E-02	1
solid material density in sediment (kg/m^3)	rhos_d	2.40 E+03	0.05
porosity of the sediment zone	beta_d	2.00 E-01	0.2
sediment burial rate (m/d)	bury_d	1.00 E-06	5
ambient environmental temperature (K)	Temp	2.83 E+02	0.02
Surface water current in m/d	current_w	3.90 E-05	1
organic carbon fraction in upper soil zone	foc_s	4.00 E-02	0.02
organic carbon fraction in vadose zone	foc_v	1.00 E-02	1
organic carbon fraction in aquifer zone	foc_q	7.50 E-03	1
organic carbon fraction in sediments	foc_d	2.00 E-02	1
bndry lyr thickness in air above soil (m)	del_ag	1.00 E-02	0.2
yearly average wind speed (m/d)	v_w	4.21 E+05	0.13

CV - coefficient of variation

Table 6. Exposure factors (Female 19+)

Description	Symbol	Mean value	CV
Body weight (kg)	BW	6.54 E+01	0.23
Surface area (m^2/kg)	SA_b	2.84 E-02	0.10
Active breathing rate (m^3/kg-h)	BR_a	7.57 E-03	0.56
Resting breathing rate (m^3/kg-h)	BR_r	4.95 E-03	0.45
Fluid Intake (L/kg-d)	I_{fl}	2.05 E-02	0.51
Fruit and vegetable intake (kg/kg-d)	I_{fv}	4.16 E-03	0.20
Grain intake (kg/kg-d)	I_g	2.74 E-03	0.20
Milk intake (kg/kg-d)	I_{mk}	3.24 E-03	0.24
Meat intake (kg/kg-d)	I_{mt}	2.28 E-03	0.24
Egg intake (kg/kg-d)	I_{egg}	3.55 E-04	0.24
Fish intake (kg/kg-d)	I_{fsh}	2.83 E-04	0.25
Soil ingestion (kg/kg-d)	I_{sl}	1.40 E-07	2.00
Breast milk ingestion by infants (kg/kg-d)	I_{bm}	0.11 E+00	0.20
Inhalation by cattle (m^3/d)	In_c	1.22 E+02	0.30
Inhalation by hens (m^3/d)	In_h	2.20 E+00	0.30
Ingestion of pasture, dairy cattle (kg{FM}/d)	I_{vdc}	8.50 E+01	0.20
Ingestion of pasture, beef cattle (kg{FM}/d)	I_{vbc}	6.00 E+01	0.40
Ingestion of pasture by hens (kg{FM}/d)	I_{vh}	1.20 E-01	0.04
Ingestion of water by dairy cattle (L/d)	Iw_{dc}	3.50 E+01	0.20
Ingestion of water by beef cattle (L/d)	Iw_{bc}	3.50 E+01	0.20
Ingestion of water by hens (L/d)	Iw_h	8.40 E-02	0.10
Ingestion of soil by cattle (kg/d)	I_{sc}	4.00 E-01	0.70
Ingestion of soil by hens (kg/d)	I_{sh}	1.30 E-05	1.00
Fraction of water needs from ground water	f_{w_gw}	8.00 E-01	0.10
Fraction of water needs from surface water	f_{w_sw}	2.00 E-01	0.10
Frctn irrgtn wtr contamnnts trnsfrd to soil	$f_{\_ir}$	2.50 E-01	1.00
Frctn frts & vgtbls that are exposed produce	$f_{abv\_grd\_v}$	4.70 E-01	0.10
Fraction of fruits and vegetables local	f_{local_v}	2.40 E-01	0.70
Fraction of grains local	f_{local_g}	1.20 E-01	0.70
Fraction of milk local	f_{local_mk}	4.00 E-01	0.7
Fraction of meat local	f_{local_mt}	4.40 E-01	0.5

Table 6. Exposure factors (Female 19+) [Cont'd]

Description	Symbol	Mean value	Coeff. Var.
Fraction of eggs local	f_{local_egg}	4.00 E-01	0.7
Fraction of fish local	f_{local_fsh}	7.00 E-01	0.3
Plant-air prttn fctr, particles, m^3/kg{FM}	K_{pa_part}	3.30 E+03	1.8
Rainsplash (mg/kg{plnt FM})/(mg/kg{soil})	rainsplash	3.40 E-03	1
Water use in the shower (L/min)	W_{shower}	8.00 E+00	0.4
Water use in the House (L/h)	W_{house}	4.00 E+01	0.4
Room ventilation rate, bathroom (m^3/min)	VR_{bath}	1.00 E+00	0.4
Room ventilation rate, house (m^3/h)	VR_{house}	7.50 E+02	0.3
Exposure time, in shower or bath (h/day)	ET_{sb}	2.70 E-01	0.6
Exposure time, active indoors (h/day)	ET_{ai}	8.00 E+00	0.14
Exposure time, outdoors at home (h/day)	ET_{ao}	3.00 E-01	0.14
Exposure time, indoors resting (h/day)	ET_{ri}	8.00 E+00	0.14
Indoor dust load (kg/m^3)	dust_in	3.00 E-08	0.4
Exposure frequency to soil on skin, (d/y)	Ef_{sl}	1.37 E+02	0.6
Soil adherence to skin (mg/cm^2)	Sl_{sk}	5.20 E-01	1.9
Ratio of indoor gas conc. to soil gas conc.	Alpha_inair	1.00 E-04	2
Exposure time swimming (h/d)	Et_{sw}	5.00 E-01	0.5
Exposure frequency, swimming (d/y)	Ef_{sw}	1.50 E+01	4
Water ingestion while swimming (L/kg-h)	I_{sww}	7.00 E-04	1
Exposure duration (years)	ED	14	1.15
Averaging time (days)	AT	2.56 E+04	0.1

Model Comparisons

We employed chemical specific data for a number of comparisons. First, DPR compared the physico-chemical (PC), intermedia transfer factor (ITF) and half-life data gathered from dozens of reports to summaries available in handbooks and in on-line sources. Second, we compared values for plant uptake from soil and biotransfer into meat and milk to standard estimation methods. Through this comparison, we demonstrate the process of data gathering and reiterate the value of experimental data. Third, we used the hexazinone data in CalTOX™ model simulations to estimate concentrations in various "on-site" media.

These estimated values were compared to data gathered from a field dissipation study in order to evaluate CalTOX™ under these conditions.

Comparison of Data Sources

We evaluated the registration data on hexazinone and a number of literature sources. A limited search of on-line data also revealed a pesticide properties database mirroring the information contained in the DPR library. The Agricultural Research Service (ARS) Pesticide Properties Database (USDA-ARS, 1997) provided accurate and extensive registrant-authored data. The United States Department of Agriculture (USDA) provided the listing. A comparison revealed data consistency between USDA and DPR library data (Table 7). We list the arithmetic mean ($\bar{x}$) for both databases (Table 7).

We considered the ARS database appropriate for the hexazinone, triclopyr and glyphosate databases. We plan to supplement this database with literature and DPR library information where needed. In addition, we plan to check any apparent outliers in the K_{ow}, VP, K_{oc} and half-life parameters for accuracy.

Table 7. Comparison of ARS to DPR pesticide properties databases

Parameter	DPR	ARS
MW (g/mol)	252.3	252.3
K_{ow} (L water/L octanol)	15	25
T_m (K)	389.2	389.2
VP (Pa)	2.2×10^{-5}	2.7×10^{-5}
S (mol/m^3)	120	130
H (Pa/m^3-mol)	2.0×10^{-7}	2.1×10^{-7}
K_{oc} (L water/kg organic carbon)	83	102
Soil, surface [T_{half_g} (days)]	110	85
Soil, root [T_{half_s} (days)]	110	85
Soil, vadose [T_{half_v} (days)]	110	85

Comparison of Biotransfer Parameters

Plants may present a significant exposure route if they contain high levels of absorbed residue but do not yet exhibit obvious herbicidal effects. Gatherers usually find dead or dying plants unappealing for basketry materials. Potential routes include plants used for food, for baskets used in food preparation or as deer or livestock forage. Because

biouptake estimations contain a large variance (see Appendix C), we carefully assess their viability as reasonable estimates. This is necessary to understand their contribution to the total variance of the exposure estimates. For these reasons, we analyzed biouptake estimation methods for plants and animals. Herbicide applications and feeding studies with animals fed treated vegetation were compared to the estimation methods.

Plant Uptake

We derived a plant/soil biouptake (K_{ps}) from total alfalfa residue and application rate information in a registrant study (DuPont, 1979). In the case illustrated by Table 8, we calculated the ratio of hexazinone in alfalfa to that in soil. Assume that soil is 1700 kg/m^3 (Hillel, 1980) and 100% of the chemical is mixed into the top 0.5 meter of soil. A biouptake parameter is then calculated using a ratio of the measured plant residue to the concentration of applied material in soil. This calculation is presented in Table 8. The application rate was 2 pounds of active ingredient applied per acre (lbs. ai/acre) in alfalfa. This rate corresponds to 0.26 parts per million (ppm) of active ingredient in soil fresh mass (ppm sFM). Table 8 lists ppm plant fresh mass (ppm pFM) and the soil/plant partition coefficient (K_{ps}). We calculate K_{ps} as the ratio of the concentration in fresh plants (ppm pFM) divided by the concentration in wet soil (ppm sFM). The arithmetic mean (and CV) of 12 experimental values is 1.2 (0.12) and compares favorably with the estimation method used by CalTOX™, which yields 1.5 (4). The equation for CV is listed below. The model predicts K_{ps} well in this case. However, using experimental data, we benefit from an improved CV (see Appendix C).

$$\mathbf{CV} = \frac{\text{arithmetic standard deviation } (s)}{\text{arithmetic mean } (\bar{x})}$$

When no K_{ps} value is available, CalTOX™ uses K_{ow} to estimate this parameter. The default variance in the estimation method corresponds to a CV of 4. While no accuracy is gained in this instance, the precision (0.12 vs. 4) improves our confidence in the result.

Table 8. Calculation of K_{ps} using 0.26 ppm hexazinone in soil on alfalfa

Location (@ 2 lbs. [1]ai/acre as 0.26 ppm [2]sFM)	**Plant Residue [ppm foliage ([3]pFM)]**	**Plant/Soil Partition Coefficient {K_{ps}} (ppm pFM/ppm sFM)**
Dover, DE	0.12	0.46
Trumansburg, NY	0.14	0.54
McFarland, CA	0.30	1.2
Visalia, CA	2.60	10
Visalia, CA	0.13	0.50
Dover, DE	0.08	0.31
Dover, DE	0.12	0.46
Dover, DE	0.07	0.27
Arbuckle, CA	0.14	0.54
Winters, CA	0.04	0.15
La Mesa, NM	0.06	0.23
Harrah, WA	0.04	0.15
Experimental average (CV)		1.2 (0.12)
CalTOXä estimation average (CV)		1.5 (4)

[1]ai-active ingredient
[2]sFM-soil fresh mass
[3]pFM-plant fresh mass

EM&PM reported concentrations in buckbrush shoots and golden fleece foliage after application of Pronone® to a Sierra Nevada national forest [Segawa, 1998 #396]. Between week 0 and week 4 (approx. 30 days) concentrations of hexazinone in plant tissue measured from non-detect to 0.98 ppm plant dry mass (pDM) in buckbrush and from non-detect to 0.80 ppm pDM in golden fleece foliage. In fresh foliage, this corresponds to 0.08 to 0.10 ppm maximum measured dry mass concentration in the first 30 days. Shoot and foliage concentration in these forest plants compares well with alfalfa values (Table 8).

Uptake into Meat and Milk

While plant uptake prediction works well for hexazinone, estimating uptake into milk and meat products is more problematic. A registrant study (Rapisarda, 1980) measured 0.01 and 0.05 ppm in goats milk from 1 and 5 ppm ^{14}C-hexazinone in feed, respectively. Just 6 percent of the radioactivity measured as the (unchanged) hexazinone parent (≈94% metabolites). However, a conservative exposure estimate assumes 100% of the residue is

the unchanged parent compound when the metabolites are not identified or their toxicities are unknown. This measurement corresponds to B_k of 0.01 ppm milk/ppm plant fresh mass (pFM). The CalTOX™ estimate, however, yielded a B_k of 3.8×10^{-7} ppm milk/ppm pFM, a five orders of magnitude difference. For the 5 ppm in feed study, the goat meat contained a concentration of radiolabeled hexazinone of 0.01 mg/kg meat. This corresponds to a meat/feed partition coefficient (B_t) of 2×10^{-3} ppm meat/ppm pFM. The CalTOX™ B_t estimation yielded 5×10^{-6} ppm meat/ppm pFM. Again, this estimation missed the mark; in this case by 3 orders of magnitude.

In summary, despite its lipophobic (fat-hating) nature, hexazinone exhibits a relatively high potential body burden from ingestion of contaminated feed. Estimation is not an exact science, especially when biological organisms are involved. This example emphasizes the necessity of obtaining experimental data, when it is available, and avoiding the pitfalls of exposure estimations based on modeling.

Estimation of Exposure Media Concentrations

In the third analysis, we compared CalTOX™ simulation results with field data gathered after a forest application in the southeastern United States. The simulation assumes hexazinone became well mixed into the root-zone soil layer following a 6.72 kg ai/ha (6 lbs. ai/acre) aerial application. Due to a lack of relevant data, however, a direct comparison of the southeastern application using CalTOX™ was not feasible. Rainfall rate, however, was extrapolated from the field study. We programmed the remainder of landscape variables (Table 5) using northern California data.

From the initial "well mixed" condition, the model predicts chemical transport between environmental media, transport out of the system (air and water movement) and transformation as removal processes. A comparison with field data gives us an idea how well the model predicts what chemical movement and degradation. Good model predictions result in similar degradation rates and inter-compartmental (e.g. between soil and plants) transfer rates that give the user some confidence that no major pathways have been excluded. Compartment (soil, air, and water) concentrations summarize the results of degradation and movement as simple values. The results of this test are presented in Table

9. While imperfect, as all models are, the overall picture shows the model predicting well for plants and soil, less well for others. The model over-predicts chemical movement into surface water while under-predicting potential sediment concentrations.

Table 9. Concentrations of hexazinone in environmental media (day 30)

Compartment (Day 30)	**CalTOX™**	**Liter-ature**	**Units**	**Citation**
Air	2.6×10^{-14}	NA	mg/m^3	NA
Plants	17	11	mg/kg(FM)	(DuPont, 1992)
Ground-surface soil	19	1.1	mg/kg(total)	(DuPont, 1992)
Root-zone soil	4.8	1.1	mg/kg(total)	(DuPont, 1992)
Vadose-zone soil	1.4×10^{-3}	0.050	mg/kg(total)	(DuPont, 1992)
Surface water	6.3	0.035	mg/L	(DuPont, 1992)
Sediment	1.0×10^{-4}	0.75	mg/kg	(DuPont, 1992)

Due to its low vapor pressure, hexazinone is unlikely to evaporate in large quantities. During spraying, only herbicide covered dust or atomized droplets are likely to contribute to inhalation exposure. Plant, ground-surface and root-zone soil concentrations are predicted well. Exposure from these compartments accounts for the vast majority of exposure to persons not in contact with the water supply. This includes traditional gatherers in California who bring their own water to a gathering site. Traditional hunter-gatherers who may use water sources near a spray site have exposure from water sources during short periods following strong rainfall events.

The differences in the CalTOX™ estimations versus those observed in the southeastern U. S. highlight the importance of site specific information when predicting chemical movement. In addition, we must account for the effect of variable application methods and buffer zones. Buffer zones are herbicide-free areas between application areas and water bodies. Buffer zones prevent herbicide runoff in all but the heaviest rainfall events. Foliar and granular formulations also behave significantly different. Streamwater monitoring by the Forest Service will provide empirical measurements to reduce the uncertainty inherent in estimating soil to stream and soil to stream sediment chemical movement.

Conclusion

This document provides a summary of preliminary efforts to quantify Native American herbicide exposure on public lands. The intermedia transfer and environmental fate models in CalTOX™ function well. However, site and application-specific information is likely to improve the accuracy of estimates. We also discussed the importance of biotransfer factors and the ability of experimental data to improve our confidence in the model result. Weaving plants for basketry and gathering forest products is sufficiently different from exposure scenarios considered by the CalTOX™ exposure model to warrant a separate assessment of dermal contact to dislodgeable foliar residues. The harvest and scouting practices of agricultural workers will serve as a surrogate model for this dermal exposure.

Important Findings: 1) Based on comparisons to field data, the scientific models provided reasonable estimates of hexazinone levels in the environment. 2) The U. S. EPA health standard, the acceptable daily intake (0.033 mg/kg-d) was 1,000 to 10,000 times higher than estimates of exposure to granular hexazinone.

We plan to continue employing CalTOX™ to estimate exposure. In addition to a separate calculation of exposure to dislodgeable plant residue, future efforts include the following:

- Gather chemical specific data for triclopyr and glyphosate
- Investigate mapping forest herbicides application areas
- Elicit weaver input on dietary and basketweaving practices in order to estimate the frequency of plant contact in gathering, processing and weaving
- Incorporate plant uptake data from the EM&PM experiments into plant contact and ingestion estimates
- Develop an exposure assessment for each chemical

We look forward to working with CIBA, U. S. EPA, the US Forest Service and EM&PM in this effort.

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Appendix A. Calculation of the Average Daily Exposure

We adopt the concentrations in air, water and soil for an exposure assessment. Those adopted are measured or estimated to be available in these environmental media at the nearest receptor point to the source (e.g., the spray area). When we assume an environmental concentration is constant over time, the population-averaged potential exposure or absorbed dose is expressed as an average daily exposure (ADE). A potential exposure is used for ingestion or inhalation routes. Absorbed dose serves as the dermal contact dosage. Expressed in mg (chemical)/kg (body weight)-day, ADE is the following:

$$\mathbf{ADE} = \sum_{i=1}^{n} \{C_i / C_k \times [IU_i / BW] \times [(EF \times ED) / AT] \times C_k\}$$

In this expression *n* represents the number of exposure media *i*. C_i / C_k is the intermedia-transfer factor. C_i / C_k expresses the ratio of contaminant concentration (C_x) of exposure media *i* (i.e., personal air, tap water, milk, soil, etc.) to a concentration in an environmental medium *k* (ambient-air gases or particles, surface soil, root-zone soil and surface water).

The expression IU_i/BW is the Intake or Uptake factor per unit body weight associated with the exposure medium. For exposure through the inhalation or ingestion route, $\{IU_i /BW\}$ is the intake rate per unit body weight per unit of the exposure medium [m^3 (air)/kg-d, L (milk)/kg-d]. For exposure through the dermal route, $\{IU_i /BW\}$ is replaced by UF_i.

The Uptake factor is measured or calculated per unit body weight and per unit initial concentration in the applied medium {L(water)/kg-d or kg(soil)/kg-d}. EF is the exposure frequency for the exposed population, in days per year. ED is the exposure duration for the exposed population, in years. AT is the averaging time for the exposed population in days.

Appendix B. Descriptions of Chemical Specific Parameters

Henry's law constant (H) is the equilibrium ratio of chemical activity in a gas over a liquid. Diffusion coefficients describe the movement of a molecule across concentration gradients. They function as variables when calculating the dispersive component of chemical transport. The higher the diffusion coefficient, the more likely a chemical is to move in response to concentration gradients. The organic-carbon partition coefficient (K_{oc}) provides a measure of chemical partitioning between organic carbon (in soils, rocks, and sediments) and water. The higher the K_{oc}, the more likely a chemical is to bind to the solid phase of soil or sediment than to the liquid phase.

The Solid-Water Distribution Coefficients

The distribution or sorption coefficient, K_d, is the concentration ratio, at equilibrium, of chemical adsorbed/adsorbed to solids and/or particles (mol/kg) to chemical concentration in the solution, mol/L. The product of K_{oc} and the fraction organic carbon in a soil or sediment is an estimate of the soil/water or sediment/water partition coefficient. CalTOX requires, as input, distribution coefficients for ground-surface, root-zone, and vadose-zone soil, ground-water-zone rock or soil, and surface-water sediments.

Biotransfer Factors and Bioconcentration Factors

The CalTOX model requires, as input, general relationships utilized to estimate partition coefficients between environmental media. These inter-media transfer pairs include: air and plants; soil and plants; animal feed intake and animal-based food products; surface water and fish; the human mother’s uptake and breast milk; skin and water; and skin uptake and concentration in skin water.

The plant-air partition coefficient, K_{pa}, represents the ratio of contaminant concentration in aboveground plant parts, in mg/kg (fresh mass), to contaminant concentration in the gas-phase of the atmosphere mg/m^3 (air). The plant-soil partition coefficient, K_{ps}, expresses the ratio of contaminant concentration in plant parts, both pasture and food, in mg/kg (plant fresh mass) to concentration in wet root-zone soil, in mg/kg.

The biotransfer factors B_t, B_k and B_e are the steady-state contaminant concentrations in, respectively, fresh meat, milk, and eggs; divided by the animals' daily contaminant intake. These factors are expressed in units of (mg/kg)/(mg/d), or (kg/d). On one hand, bioconcentration factors express steady-state concentration ratios between animal tissue and a specific environmental medium. Unlike bioconcentration factors, biotransfer factors express the steady-state relationship between intake and tissue or food-product concentrations.

Lactating women can transfer to breast milk a portion of the contaminants they absorb from all intake routes—ingestion, inhalation, and dermal contact. B_{bmk} is the biotransfer factor for milk-concentration versus the mother's intake. This relationship is described as the ratio of contaminant concentration in mother's milk divided by the mother's daily intake of that contaminant, in units of $\frac{mg/L\,(\text{milk})}{mg\,(\text{in feed})/day}$ or days/ L (milk).

The bioconcentration factor (BCF) provides a measure of chemical partitioning between fish tissue based on chemical concentration in water.

Chemical specific exposure factors include the skin-water and skin-soil partition coefficients in CalTOX. K_m is the skin-water partition coefficient in cm^3 (water)/cm^3 (skin). In order to estimate the skin-soil partition factor, K_m^{soil} , with units cm^3(soil)/cm^3(skin), we divide K_m by the sorption coefficient K_d for soil, or

$$\mathbf{K_m^{soil} = \frac{K_m}{K_d}}$$

K_{p_w} is the steady-state water/skin permeability coefficient in cm/hour. In other words, the parameter is a contaminant flux from water through the skin's stratum corneum. The value is derived using measurements or an estimation method.

Chemical-Specific Transformation Process Half-Lives

Chemical transformations, which may occur as a result of biotic or abiotic processes, can have a profound effect on the persistence of contaminants in the environment. Experimental methods and estimation methods are available for defining these fate processes in a variety of media. Specific information on the rates and pathways of

transformation for individual chemicals of concern should be obtained directly from experimental determinations, if possible, or derived indirectly from information on chemicals that are structurally similar. CalTOX adopts media- and reaction-specific reaction half-lives to establish rate constants for transformation removal processes that include photolysis, hydrolysis, oxidation/reduction, and microbial degradation.

Transformation rates half-lives are among the more uncertain parameters in the CalTOX model. There are typically few available measurements or ranges of estimated values in the primary and secondary literature. Most of the available half-life values are obtained from limited measurements for environmental media that are not necessarily representative of those in California. These values often involve scientific judgment as much as measurement. In making use of these data, we expanded the range of the reported values by a factor of 5 when only 2 or 3 representative values are presented and by a factor of 10 when only one value is provided. If 4 or more measured values are available, these uncertainty factors are not applied. In order to express the lack of reliability associated with a limited number of measured values for a parameter, these uncertainty factors are used to express both large uncertainty and significant variability.

Appendix C. Interpreting Variance in Environmental Models

We calculate variance in environmental measurements and model estimations and rely on this important factor to describe our confidence in a value. We traditionally break variance into at least two sources: uncertainty and variability. Some variance occurs due to errors in measurement (*uncertainty*) or in the natural range in values occurring in a population (*variability).* Variance is the sum of uncertainty and variability.

For example, samples of dioxin contaminated sediment vary from sample to sample to due measurement error (uncertainty) and from sample to sample (variability). These samples may contain values ranging from 0.01 to 10 parts per billion dry sediment (μg/kg) with a mean of 1 ppb and a standard deviation of 5 ppb. While a defined volume of sediment has a theoretical average concentration, grab samples contain measurable concentrations that vary in time and space. This temporal and spatial variability is inherent. We calculate the coefficient of variation {standard deviation/mean} and get 0.2. This value is typical of concentration measurements under field or biological systems but high for variance in analytical applications. With laboratory measurements, where variance reflects random error and the limitations of a particular method, we expect a range of $0.01<CV< 0.1$.

The problem of variance amplifies when measuring intermedia transfers. Because we measure at least two media, say soil and plant tissue, the variance may be multiplied. If both soil and plant tissue contain a coefficient of variation of 1.4, the resulting combined variance may be as much as 1.4^2 or 2. The outcome is less predictable when we put models to use in estimating a parameter.

Models also contain variance. Simple regression models, for example, contain variance in the estimate of the slope. When estimating physico-chemical or biotransfer parameter, CalTOX™ employs simple models [McKone, 1994]. A large set of measured values helps predict an unknown parameter using a statistical relationship. We evaluate the relationship between the measured and unknown value. This relationship often contains significant error. For example, bioconcentration of the chemical ChemicalX (Cx) into fish (BCF) is estimated using a standard partition ratio called K_{ow} (octanol/water partition coefficient).

ChemicalX, when dissolved in a flask containing octanol and water, dissolves in octanol 100 times better than water (K_{ow} = 100). When measured octanol-water partition coefficients are plotted against measured BCF's for many similar chemicals, a linear relationship is established. This hypothetical model gives us the equation:

$$\mathbf{BCF = 0.048 \times K_{ow} \quad SE = 20}$$

where SE is the standard error in the predicted value (BCF). We predict BCF for Cx using its measured K_{ow} (if K_{ow} falls within the linear range of the model). The estimated BCF is $\{0.048 \times 100\}$ or 4.8. In this example, we are uncertain about (1) the measurements of both BCF and K_{ow} (uncertainty) used in the model, (2) how appropriate the model is for ChemicalX, and (3) the estimate of the slope. While certain aspects of the variance are very difficult to quantify (model variance for example), there are ways to reduce total variance.

We can reduce the variance in a predictive model. The ideal model for ChemicalX would use BCF and K_{ow} measurements of a series of chemically similar compounds in the fish species of interest. This information, however, is rarely available and a large collection of similar and dissimilar organic chemicals is often used to derive the relationship. In practice, we find that variance in landscape and exposure factors are small relative to physicochemical, biotransfer and half-life parameters (Currie, 1995).

We imagine, then, how uncertain our model world is. Estimating movement of ChemicalX from a spray site to edible fish includes three media and their corresponding half-lives (soil-surface $\Rightarrow$ water $\Rightarrow$ fish), two intermedia transfers (soil-water, water-fish) and many other factors. Each factor dilutes and partitions the chemical in the water, biota and soil environments. Variance in the multimedia model result, then, depends highly on the most sensitive parameter (see pgs. 12-13), and may range $5 < CV < 10$. Interpreting the model result and its variance, then, depends on the situation, the parameter, and ultimately the extent of our knowledge.